

although new states do appear in the bulk bandgap, they overlap those from the valence and conduction bands (Fig.5.31). It will be further seen that this band structure resembles that of zig-zag and armchair graphene-like nanotubes although the bandgap value is still closer to that of würtzite nanotube; this bandgap value is expected to increase if the structure would be relaxed further.

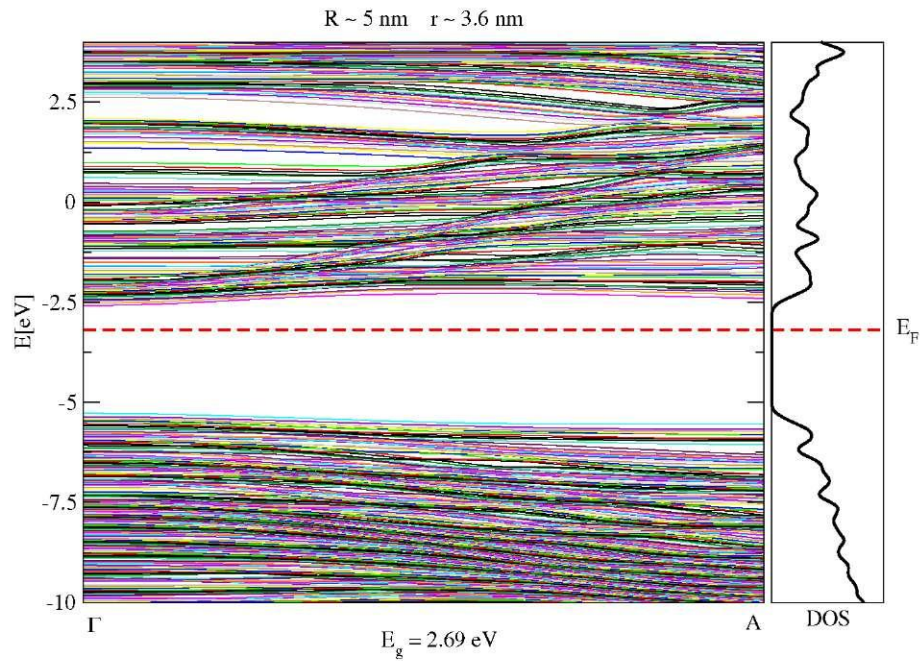


Figure 5.31: Band structure and DOS for the $R = 5$ nm, $r = 3.6$ nm nanotube

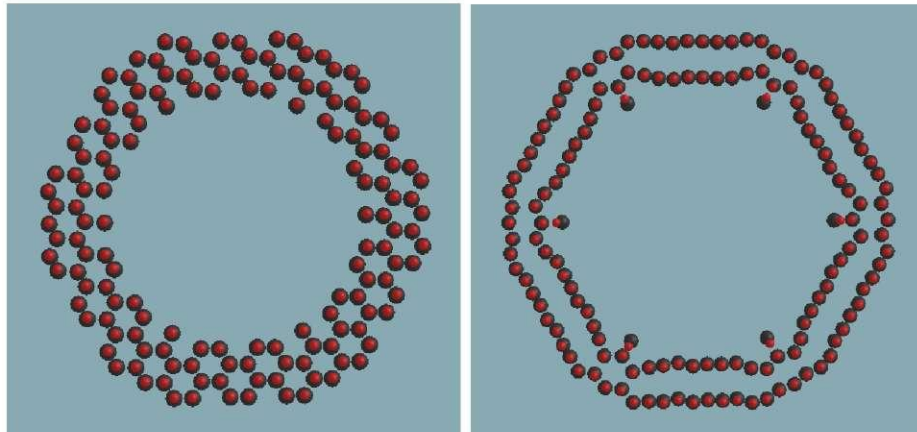


Figure 5.32: Initial and relaxed atomic positions for the $R = 5$ nm, $r = 3.6$ nm nanotube

The next two examples are those of nanotubes similar in structure to single walled carbon nanotubes and the main purpose for their investigation is to further confirm the validity of the results by comparing their properties with other numerical simulations and experimental data. The two structures chosen were that of a hexagonal zig-zag BN nanotube (Fig.5.34) with a diameter of 0.94 nm and a hexagonal armchair nanotube (Fig.5.36) with a diameter of 0.82 nm. The bandgap values of both zig-zag (Fig.5.33) and armchair (Fig.5.35) nanotubes are found to be in good agreement with experimental results ([31]) with a value of 4.23 eV in the case of the zig-zag structure and 4.45 eV for the armchair nanotube. A lack of any narrow mini-bands inside the bandgap can be seen, as in the case of the $R = 5$ nm $r = 3.6$ nm nanotube (Fig.5.31).

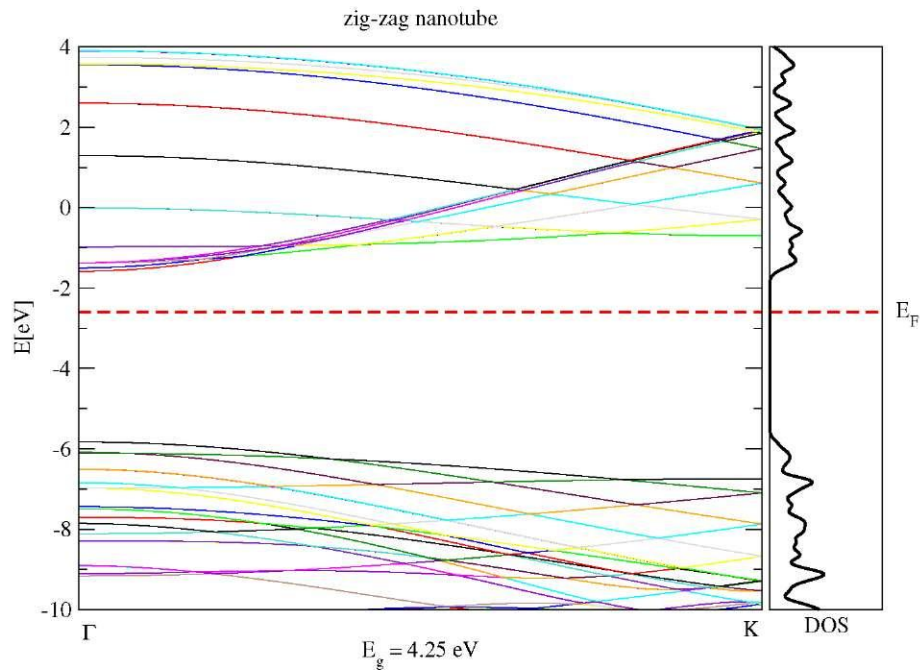


Figure 5.33: Bands structure of a graphene-like zig-zag BN nanotube

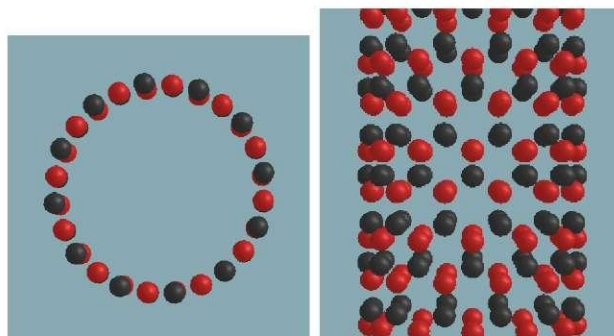


Figure 5.34: Initial and relaxed atomic positions for the graphene-like zig-zag BN nanotube

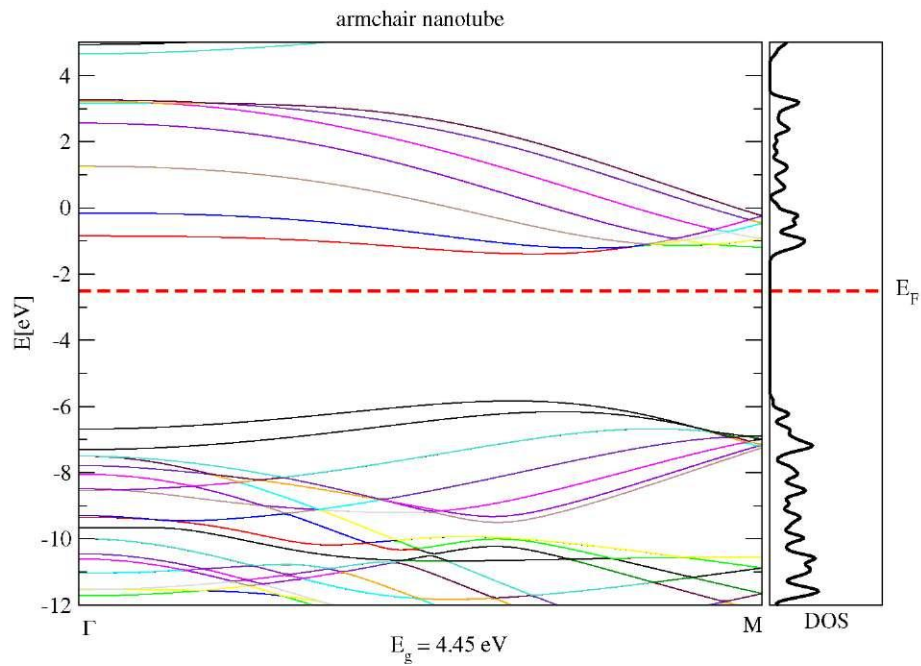


Figure 5.35: Bands structure of a graphene-like armchair BN nanotube

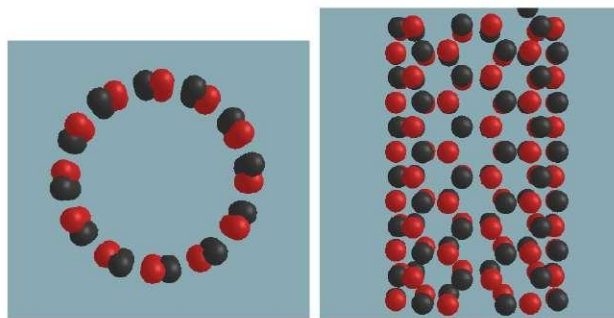


Figure 5.36: Initial and relaxed atomic positions for the graphene-like armchair BN nanotube

5.5 Stability of the structures

By comparing the energy per atom ratio for the different structures it is possible to identify those with a more stable structure, which also translates with a higher probability of being synthesized to the detriment of others.

Structure type	energy per atom [eV]
Bulk	-180.911
R – 2 nm r – 0 nm	-180.438
R – 2 nm r – 1 nm	-180.123
R – 3.3 nm r – 0 nm	-180.484
R – 3.3 nm r – 1.3 nm	-180.400
R – 3.3 nm r – 2 nm	-180.221
R – 3.3 nm r – 0 nm e.s.*	-180.534
R – 3.3 nm r – 1.3 nm e.s.*	-180.469
R – 3.3 nm r – 2 nm e.s.*	-180.318
R – 5 nm r – 3.6 nm	-180.532
zig-zag	-180.692
armchair	-180.669

(* e.s. – enhanced surface which refers to the base being enhanced for the surface treatment; R – external radius, r – internal radius)

It can be seen that that the bulk crystal remains the most stable of them all; the zig-zag and armchair graphene-like structures come second; the largest nanotube (R – 5 nm, r – 3.6 nm) that switched from a würtzite type to a graphene-like nanotube structure, although it went through the least number of relaxation steps out of the entire set of structures, also shows a stable structure; out of the würtzite structures, the nanowires remain more stable than the nanotubes of similar external diameter and in the case of the tubular structures, the stability decreases with the increase of internal diameter.

5.6 Phonon dispersion

Another set of differences between q-1D structures and bulk BN material can also be seen by analyzing the phonon dispersion. Due to computational constraints, only some of the structures mentioned up until now have been studied further in this section. The method used to obtain the phonon dispersion was mentioned in Section 4.5 but an additional program entitled "vib2axsf", that was developed by Andrei Postnikov, and that is also part of the SIESTA package was used to graphically represent the first six phonon modes starting from frequency $0[cm^{-1}]$ upwards in order to have a visually clear proof of the differences between them; the reason for choosing the first six modes is just that these are the simpler ones to understand in terms of the motion of the constituent atoms.

In Fig.5.37 the BN bulk phonon frequencies (in the Γ point), as computed in [32], have been superimposed over a part of the phonon dispersion graph of the BN würtzite R – 2 nm nanowire. It can be clearly seen that a dramatic deviation from the bulk behavior takes place and that there is an almost continuous spectrum of modes up until $1250[cm^{-1}]$; this deviation from the reduced number of phonon modes found in the bulk material is an effect given by the 1D confinement, the new symmetry of the system and surface relaxation effects that lifts the degeneracy of equivalent modes that can be found in the bulk material but also gives rise to new class of phonon modes without any bulk counterparts. An important observation is that the usual gap (for the dispersion along the Γ -A direction) between the bulk LO_{\parallel} and TO_{\perp} values vanishes. The phonon modes that can be found above the $1320[cm^{-1}]$ frequency appear due to the relaxation of the outer atomic layer (Fig.5.38) that leads to a higher force constant for between some of these atoms which translates to a higher frequency of oscillation for these surface phonons. The phonon modes found just above the $1350[cm^{-1}]$ appear to have nondisper-

sive behavior. The modes found above $1400[\text{cm}^{-1}]$ are of a mixed type, with both atoms found on the surface and inside the nanowire taking part in the oscillation, but the major contribution is still that from surface. All the surface modes appear to have a longitudinal polarization, parallel to nanowire's optical axis, since the great majority of the atoms, but not all, oscillate in such a way.

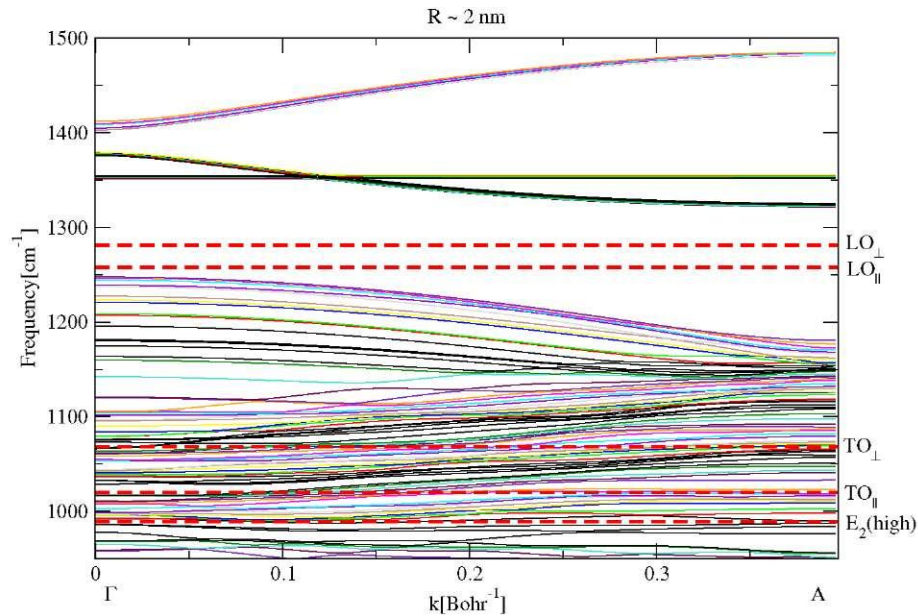


Figure 5.37: Phonon dispersion for $R = 2$ nm wurtzite nanowire with superimposed bulk modes

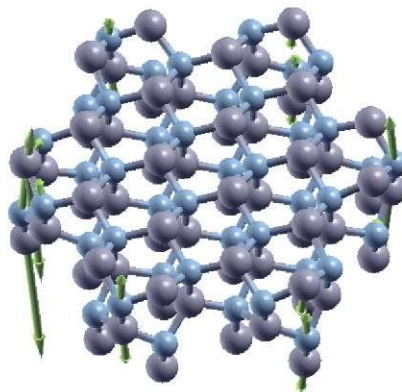


Figure 5.38: Graphical representation of force vector/atom for a surface phonon

In order to have a visual representation of the phonon modes found in a BN nanowire, the first six have been represented in Fig.5.39. Even amongst these very few number of modes there are examples of degeneracy lifting and new, confinement deter-